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Pesticides residues on Loquat: A minor crop in Lebanon

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ABSTRACT

Loquat in Lebanon is subjected to sprays by a variety of unregistered pesticides, as is the case with minor crops in many parts of the world, to protect it from pests mainly scab. This malpractice would raise consumer's health safety issues related to pesticides residues that could be avoided if the pesticides industry worldwide is not reluctant in investing in the registration of minor crops pesticides. Penconazole is registered as a fungicide against scab on apples and pears in Lebanon without prior supervised field trials, but it is not registered on loquat.

The aims of this study are to screen and quantify the range of pesticide residues in 128 loquat samples gathered from Lebanese market between 2017 and 2019, study the dissipation behavior of penconazole on apple and loquat in the field, confirm the critical good agricultural practices (cGAP) of penconazole on apples and propose a pre-harvest interval (PHI) for penconazole on Loquat in Lebanon.

The samples were analyzed using a validated MRM method on apple with GC-MS/MS and LC-MS/MS determination. A total of 51 samples were irregular in terms of the pesticides residues found, with, residues of unauthorized pesticides detected on 48 samples. The most frequently encountered unauthorized pesticides banned in Lebanon were: cypermethrin (10.9%), dimethoate (6.25%), methomyl (6.25%), carbendazim (3.1%), and thiametoxam (2.3%). Penconazole dissipated following a first order kinetic dissipation model on apple and loquat. The half-life calculated on apple and loquat were 8.56 days and 9.49 days, respectively. A PHI = 14 days can be proposed for loquat with a MRL of 0.07 mg/kg without any food safety issues raised with the same cGAP practiced on apple.

1. Introduction

Three global minor use summits (Global Minor Use portal, 2019), IR4 project in Northern America (Baron, Holm, Kunkel, Schwartz, & Markle, 2016), Specific Off Label Approval (SOLA) in UK (Hillocks, 2012), European Union MU data base (EUMUDA) and "coordinated IPM in Europe program" (Lamichhane et al., 2015) and many regulations are all part of the worldwide effort to address the different facets of the "minor crop problem". "Minor uses are those uses of plant protection products (defined in relation to crops and pests) in which either the crop is considered to be of low economic importance at a national level (minor crop), or the pest is of limited importance on a major crop (minor pest)" (EPPO, 2007). Although organizations differentiate between minor crops and minor uses, the basic issue revolves around the availability of sufficient safe and effective pesticides registered for use on specialized crops (Baron et al., 2016). This unavailability is created by the reluctance of the pesticides industry to invest in minor crops and minor use registration, and to hold additional concomitant liability as an outcome of new registrations, with no justified revenue returns (Fennimore & Doohan, 2008; Kunkel, 2012). Farmers, on the other hand, challenged by pests threatening their produce (Fennimore & Doohan, 2008), find themselves obliged to use unauthorized pesticides.

Loquat, *Eriobotrya japonica* Lind. is an evergreen of the Rosaceae family with 3 vegetative flushes a year and harvest during spring. It is a subtropical tree, widespread in the Mediterranean region (Llácer, G., Badenes, M. L., &), with only small areas of production, which makes

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the description of minor crop very suitable (EUROPEAN COMMISSION, 2017). In Lebanon, it only occupies about 426.2 ha out of 230,000 ha of the total cultivated areas and is concentrated in South Lebanon in an area of 348.3 ha, while the other 75 ha are spread all over Lebanon (Lebanese Ministry of Agriculture/FAO, 2017). Though it is considered a minor crop, it has a certain economic importance as its produce is not only consumed locally as a fruit delicacy but is also exported to regional markets, which have become increasingly demanding in terms of compliance to pesticide residues safe limits.

Loquat's growing habit of flourishing in high humidity microclimates and soils makes it prone to a variety of pests, mainly the most detrimental apple scab *Venturia inaequalis* (González-Domínguez, Armengol, & Rossi, 2017).

Due to the fact that difenoconazole is the only pesticide registered in Lebanon on loquat, Loquat has earned the title of being an orphan crop in the sense that not enough pesticides are registered on it to control its pests (Lebanese Ministry of Agriculture, 2019). To avoid huge economic losses of their crop, Lebanese growers spray all kinds of fungicides and insecticides known to chemically control scab and fruit flies, regardless of whether or not these pesticides are authorized for use on Loquat.

Similarly, other growers of the world seem agonizing of the same dilemma. Yang, Luo, Li, & Liu, 2016 found that 65.0% of all samples analyzed of minor crops in China, mainly starfruits, crab apple, and Indian Jujube, were irregular in terms of pesticides residues detected (Yang et al., 2016). These samples contained at least one of the following non-authorized pesticides: carbendazim, imidacloprid, chlorbenzuron, and iprodione (Yang et al., 2016). Moreover, by mean of the Article 31 of Regulation (EC) No. 396/2005, Italy reported in 2017, 109 (0.9%) incompliant samples with the EU Maximum Residue Limits (MRLs) out of a total of 11,497 samples food samples tested. The only loquat sample tested out of the 109 total samples had dimethoate residues exceeding the EU MRL (EFSA, 2019). Sangur et al., 2012 investigating pesticides residues in fruits and vegetables in Hatay region Turkey, found carbendazim in 30% of the tested loquat samples (Sungur & Tunur, 2012).

Yang et al., 2016 stated that hardships are eminent for producers lacking authorized plant protection products with regulatory neglect (Yang et al., 2016). Accordingly, it would be desirable to equip the Lebanese farmers with registered chemical pesticides to use safely on loquat, especially members of the triazoles family, which are known to curatively control scab. But, at the same time, because repeated uses of triazoles induce resistance in scab, registering fungicides with different modes of action to be alternatively used will help in resistance management.

Extrapolation of pesticides good agricultural practices (GAP) from a major crop to a minor crop through a reduced number of supervised field trials and bridging studies among crop groups is the main common approach recognized by the regulatory authorities and recommended by the Organization for Economic Co-operation and Development (OECD) (OECD, 2016), European Union (EUROPEAN COMMISSION, 2017) and FAO (FAO, 2016) to tackle the problem of minor crops.

Penconazole is a fungicide, belonging to the triazoles family, used to control scab on pomefruits (apple, pear), including loquat in many parts of the world. Nevertheless, in Lebanon, penconazole is registered only on apple and pear by adoption of the cGAP of Spain, without conducting supervised field trials as it is a customary practice in Lebanese registration to follow the registration of a reference country. The Maximum Residue Limit adopted by the EC for penconazole on pomefruits is 0.15 mg/kg, while that on loquat is 0.07 mg/kg (European Commission, 2020). In Lebanon, The MRL officially adopted for penconazole on apple is 0.1 mg/kg as listed in the Codex Alimentarius (FAO/WHO, 2017) while no MRL for loquat has been specified. Regardless of how sound this practice is, if there were pesticides residues trials conducted on apple, occupying an area of 14,300 ha and total production of 160,000 tons/year (Lebanese Ministry of Agriculture/FAO, 2017), then the expansion of the label to include loquat can be done by extrapolation with a minimum number of 3 trials on loquat, as apple is the representative of the commodity group that includes both apple and Loquat (EUROPEAN COMMISSION, 2017). Bearing in mind what Ripley et al. (Ripley, Ritcey, Harris, Denommé, & Lissemore, 2003) concluded in their study that pesticide recommendations cannot always be extended to specialty crops without an investigation of the changes in preharvest intervals to prevent violations of the maximum residue limits.

The aims of this study are to screen and quantify the range of pesticides residues in loquat samples from Lebanese market, study the dissipation behavior of penconazole on apple and loquat, confirm the cGAP of penconazole on apples and propose a pre-harvest interval (PHI) for penconazole on loquat in Lebanon.

2. Materials and methods

2.1. Chemicals and reagents

The reagents used were of analytical grade. The pesticide standards of high purity grades (>99%) were purchased from Dr. Ehrenstorfer (Augsburg, Germany). Individual stock solutions were prepared at 1000 mg/L in acetonitrile and stored at −20 °C. HPLC grade acetonitrile was obtained from VWR CHEMICALS (Fontenay-sous-Bois France). Ethyl acetate was obtained from Scharlab (Sentmenat, Spain). Phenomenex roQ QuECHERS kit EN 15662 method packet (4.0 g magnesium sulfate, 1.0 g sodium chloride, 1.0 g sodium citrate tribasic dihydrate, 0.5 g sodium citrate dibasic sesquihydrate) and Phenomenex roQ QuECHERS dSPE kit-15 mL CT (900 mg MgSO4, 150 mg PSA) were obtained from Torrance, USA. Topas pesticide formulation (penconazole 10% EC) was purchased from Syngenta.

2.2. Sampling

For the purpose of screening pesticide residues on loquat, a total of 128 loquat samples were collected randomly over a period of 3 years from 2017 till 2019 from orchards, wholesale markets, retail shops, and packing houses of fruits meant for export.

Concerning the dissipation and normal studies, sampling was carried following the FAO guidelines, "Submission and evaluation of pesticide residues data for the estimation of maximum residue levels in food and feed" 2016. Each sample consisted of 12 fruits of apples or the equivalent of 2 kg of apple or loquat with size and quality ready for harvesting. For the dissipation studies on apple and loquat, 3 field replicates were taken at intervals 0 + 2 h, 1, 2, 6, 9, 14 and 21 days after the 3rd pesticide application. For normal studies on apple and loquat, two field replicate samples were taken at intervals 0 + 2 h and 14 days from the control and the treated plots.

2.3. Sample preparation: QuEChERS extraction

To ensure a quick and easy sample treatment, a modified QuEChERS (quick, easy, cheap, effective, rugged and safe) method was used. This method was originally developed as a powerful sample preparation to analyze hundreds of pesticides residues in different kinds of food samples. The whole 2 kg field samples of whole apple and Loquat fruits were homogenized thoroughly. Ten g of the homogenized sample was weighted in a 50 mL centrifuge tube. An aliquot of 10 mL of acetonitrile (ACN) was added to the sample, then hand-shaken vigorously for 1 min. A packet of Phenomenex roQ QuECHERS kit EN 15662 method was added to the tube, which was then sealed tightly, hand-shaken vigorously for 1 min, then centrifuged for 5 min at 5000 rpm. A 6 mL aliquot of the upper ACN layer was transferred into a Phenomenex roQ QuECHERS dSPE kit-15 mL tube; the tube was tightly capped and hand-shaken for 30 s. The 15 mL tube was centrifuged for 5 min at 5000 rpm. 300 μL of the upper layer were then filtered through 0.45 μm polyvinylidene fluoride (PVDF) syringes filter into 1.5 mL vials, dried by N2 flow and reconstituted with ethyl acetate for GC analysis. Prior to

Table 1
Location, trial type, and experimental conditions and parameters *(Meier et al., 1994),**(Martínez-Calvo et al., 1999).

Type of trial	Location	Start date	End date	T (°C)	Av. relative Humidity	Variety	Spray volume in L at 3rd application	Av. fruit weight (g)	Growth stage (BBCH)*,**
Apple									
Dissipation	Kfardebian	9/8/2017	19/9/2017	19–29	55–57	Red starking	60	180	81
Normal	Aammiq	22/8/2017	25/9/2017	19–29	55–57	Golden Delicious	100	160	84
Normal	Qartaba	5/9/2017	10/10/2017	13–27	50–56	Super chief	16	180	89
Normal	Qartaba	5/9/2017	10/10/2017	13–27	50–56	Golden delicious	20	160	89
Normal	Kfardebian	8/9/2017	11/10/2017	16–27	55–56	Scarlet spur	80	180	81
Normal	Kfardebian	8/9/2017	11/10/2017	16–27	55–56	Double red	80	185	81
Loquat									
Dissipation	Zoghdraya	19/3/2018	9/4/2018	9–20	58–63	Baladi	85	28	807
Normal	Darb-as-sim	28/2/2018	2/4/2018	9–20	58–63	Turkish	30	41	709
Normal	Darb-as-sim	28/2/2018	2/4/2018	9–20	58–63	Spanish	68	32	708

injections, 9 μL of tri-phenyl phosphate (TPP) were added as injection internal standard (I-IS).

2.4. Pesticide residue determination: GCMSMS and LCMSMS

GC-MS/MS analyses were carried out with an Agilent 7890A GC equipped with 7693 Agilent Auto-sampler and 7000C Triple Quadrupole GC/MS system from Agilent technologies (Santa Clara, California, USA). The separation was performed on a HP-5 MS column, 0.25 mm internal diameter × 30 m length, 0.25 μm particle size. Helium (purity 99.996%) was used as a carrier gas at a constant pressure of 11 psi. The inlet temperature was set at 250 °C; the mode of inlet was splitless; the injection volume was 1 μL. The column temperature program was as follows: the initial temperature was maintained at 70 °C for 1 min, increased to 160 °C at a rate of 50 °C/min, raised to 200 °C at 2 °C/min, raised at 16 °C/min up to 280 °C and held there for 7.2 min. The total run time was 35 min. The mass spectrometer was operated with an electron impact (EI) source in multiple reactions monitoring (MRM) mode. The electron energy was 70 eV and the source, transfer line and quadrupole temperatures were set at 280 °C and 150 °C, respectively. In order to prevent instrument damage, the solvent delay was set at 4.5 min. The optimized parameters for penconazole are as follows: retention time 18.7 min, quantitative transition 248 > 192, and qualitative transition 248 > 157. An ion ratio percentage of 30% tolerance was used for both standards and samples.

LC-MS/MS analyses were carried out with an Agilent 1200 HPLC equipped with 3200 QTrap Triple Quadrupole Ion Trap system from AB Sciex. The separation was performed on an Agilent Column Zorbax Eclipse plus C18 Analytical, 4.6 mm internal diameter × 150 mm length, 5 μm particle size. The solvents used were: Solvent A (water +20%

Table 2
Chromatographic conditions, Validation and MS parameters of 14 chemical classes representative analytes out of 76.

Analyte	RT (min)	Q1	Q3	CE (ev)	Spiked level (mg/kg)	Recovery	RSD (%,n = 10)	Matrix effect %	Correlation coefficient
Acetamipride	10.9	223	126.1	27	0.01	96.15	14.53	8.0	0.9998
		223	73	75	0.05	81.88	2.86		
azoxystrobin	16.1	404.1	371.9	10	0.01	96.12	13.46	6.1	0.9998
		404.1	344	19	0.05	80.22	3.05		
carbendazim	12.1	192.082	160.1	19	0.01	96.07	6.05	16.6	0.9997
		192.082	132.2	37	0.05	78.86	9.39		
chlorpyrifos	16.28	313.8	258	14	0.01	103.6	17.31	2.7	0.9998
		314	286	5	0.05	82.28	4.88		
cyflufenamid	24.26	188.1	88	35	0.01	74.44	18.46	1.7	0.9997
		118.1	89	25	0.05	73.58	2.94		
cymoxanil	11.6	199.164	127.9	13	0.01	110.41	12.13	4.5	0.9991
		199.164	83	19	0.05	85	3.33		
dimethoate	11.1	230.08	125.1	25	0.01	106.52	13.91	0.9	0.9998
		230.08	199	13	0.05	87.22	2.57		
Diflubenzuron	18.5	311.03	158.1	17	0.01	109.55	11	7.2	0.9996
		311.03	141	39	0.05	87.16	5.71		
flutriafol	21.15	219	123.1	12	0.01	95.6	6.43	0.7	0.9992
		219	95	20	0.05	75.46	3.23		
Fluazinam	20.3	466.1	173	27	0.01	92.9125	18.52	8.2	0.9997
		466.1	174	29	0.05	73.28	5.16		
metalaxyl	14.16	249	146	20	0.01	9.58	4.81	0.1	0.9997
		160	130	20	0.05	75.4	3.14		
methomyl	9.4	163	88	13	0.01	91.36	4.77	3.7	0.9999
		163	106	13	0.05	77.46	4.32		
myclobutanil	23.22	179	125	14	0.01	93.72	4.77	9.0	0.9997
		179	152	6	0.05	81.32	5.82		
pendimethalin	18.34	252.1	162.1	10	0.01	102.68	11.6	0.7	0.9994
		252.1	161.2	20	0.05	76.54	5.8		

Methanol+ 5 mM Ammonium Acetate) and solvent B (Methanol + 5 mM Ammonium Acetate). The injection volume was 10 μL. The total run time was 30 min. The mass spectrometer was operated with an electro Spraying ionisation (ESI) source in multiple reactions monitoring (MRM) mode. The optimized parameters for penconazole are as follows: retention time 18.4 min, quantitative transition 284.344 > 159.1 and qualitative transition 284.34 > 69.9. An ion ratio percentage of 30% tolerance was used for both standards and samples.

2.5. Trials and spraying technique on apples and loquats

During the years 2017 and 2018, one dissipation and 5 normal pesticide field trials were conducted on apples in 3 different locations in Mount-Lebanon and Beqaa. In addition, one dissipation and 2 normal field trials were conducted on loquat in 2 different locations in East Sidon, the main area of loquat production, South Lebanon. The trials plots were managed following local agricultural practices, including irrigation, fertilization, pest control and other practices to ensure good crop production. The Guidelines on comparability, extrapolation, group tolerances and data requirements for setting MRLs SANCO 7525/VI/95 Rev. 10.2 September 23, 2016 and OECD guideline 509 and its Guidance document on crop field trials (Series on Pesticides No. 66) were followed. A single un-replicated plot design was used. Each of the treated and the control plots was made of 6 trees of the same variety, separated by a buffer zone of, at least, 15–20 m, in commercially grown orchards. All the conditions and parameters related to the field trials are summarized in Table 1.

The same GAP adopted by Lebanon for penconazole on apples was followed in all the trials. It consisted of spraying thrice at 10 days interval from −20, −10, and 0 days from sampling at a rate of 50 mL of the commercial formulation/100 L of water and a PHI = 14 days. At each site, commercial application of the pesticide was simulated using the available spray equipment that varied between a tractor driven pump with a hand gun in Aammiq, a motorized back sprayer in Qartaba, and most commonly used handgun attached to a portable motorized pump in the rest of the trials. Before application, the spray equipment was checked for delivery rate that was recorded. For each treatment, clean tanks with clean hoses were used to dilute and spray the fungicide immediately. A fine spray targeted the foliage to a thorough coverage until dripping. No sprays were made when it was raining or when wind speed was more than 10 km/h.

2.6. Statistical analysis

Data were statistically evaluated using Excel and IBM SPSS 22.0 (statistical package for social sciences). The penconazole residues values from the dissipation studies on apple and loquat were best fitted to a first-order kinetics, $C = C_0\ e^{-kt}$, employing a nonlinear least-squares regression analysis of residue concentration against time. To ascertain if datasets originating from apple and loquat residues come from populations characterized by similar mean and variance, statistical tool (Mann-whitney *U* Test) was used.

3. Performance of the analytical method

Originally, validation experiments have been performed in both LC–MS/MS and GC–MS/MS analytical systems to prove suitability of the multi-residue analysis method to test for 76 pesticides analytes in apple, the group representative of loquat. Performance of the used analytical method was evaluated by checking validation parameters and acceptance criteria, following SANCO guidelines on "ANALYTICAL QUALITY CONTROL AND METHOD VALIDATION PROCEDURES FOR PESTICIDE RESIDUES ANALYSIS IN FOOD AND FEED Nº SANTE/12682/2019".

Linearity check was performed by plotting calibration curves of the peak area against a range of 7 concentrations (0.01–0.5 mg/L) of a mixture of 76 pesticides analytes in Acetonitrile with n = 10 replicates of the target analyte. Acceptability was conditioned for correlation coefficient R2≥0.98. All the correlation coefficient of the calibration curve of the 76 analytes varied between 0.9991 and 1 demonstrating a very good linearity (Table 2).

The accuracy was assessed from the recovery of the pesticides analytes at 2 levels of fortification: 0.01 mg/kg and 0.05 mg/kg. The recoveries of all tested analytes varied between the lowest 73% for proquinazid to 112% for etoxazole at 0.01 mg/kg level, and 70.44% for tolfenpyrad and 90.56% for etoxazole at 0.05 mg/kg level. The results indicate satisfactory method performance in terms of recovery as shown in Table 2.

Precision of the method was evaluated by assessing repeatability and reproducibility through the calculation of the relative standard deviation on test results for 10 replicates at 2 spiked levels. The lowest RSD at 0.01 mg/kg spiked level was calculated as 4.49 for pirimicarb, while the highest calculated was 18.52 for fluazinam. The lowest RSD calculated at 0.05 mg/kg was for diazinon, while the highest was for thiabendazole with a value of 13.04 (Table 2). All the calculated RSD for the different analytes were less 20%, indicating a very good repeatability of the method. As an important step in the verification process, the matrix effect was investigated by comparing calibration of pesticides analyte standards dissolved in solvent with matrix-matched standards. Percentage matrix effect was calculated using the following equation:

$$\%\ \mathrm{ME} = \ \mathrm{RSD} = 100 * \frac{\textit{Standard deviation between the slopes of the calib. curve in solvent and the matrix}}{\textit{mean of the slopes of analyte in solvent and in matrix}}$$

The matrix effect varied between the lowest value of 0.11 for metalaxyl and 16.67 for carbendazim (Table 2). It is considered that there is no matrix effect if the % is ≤ 20% in accordance with SANCO guidelines.

4. Results and discussion

4.1. Screening results of loquat samples

Out of the 128 samples of loquat tested for pesticides residues, 51 samples were contaminated (Table 3) among which 48 samples held residues of unauthorized pesticides, indicating that the Good Agricultural Practices (GAP) may not be well followed in Lebanon (Yu et al., 2017). The other 77 samples were compliant, 12 samples of which contained residues of difenoconazole, the only registered pesticide on loquat in Lebanon with levels below the MRL. No residues were detected at all in the other 65 samples.

The most frequently encountered unauthorized pesticides detected are listed as percentage of the total number of samples tested: cypermethrin (10.9%) with concentrations ranging from 0.021 to 0.136 mg/kg, dimethoate (6.25%) with concentrations ranging from 0.0153 to 0.595 mg/kg, methomyl (6.25%) with concentrations ranging from 0.0162 to 0.0518 mg/kg, carbendazim (3.1%) with concentrations ranging from 0.08 to 0.0963 mg/kg, and thiametoxam (2.3%) with concentrations ranging from 0.017 to 0.062 mg/kg. It is worthy to note that these pesticides are now banned in Lebanon. Though cypermethrin,

Table 3
Screening results of 128 loquat samples for pesticides residues.

Loquatsamples = 128	cypermethrin	dimethoate	methomyl	Flutriafol	carbendazim	cyflufenamid	chlorpyrifos	thiametoxam	tebuconazole	mandipropamide	azoxystrobin	tetraconazole	metalaxyl	lambda − cyhalothrin	isopyrazam	myclobutanil	deltamethrin	Thiophanate − methyl	cymoxanil
EU-MRL[d]	1	0.01	0.01	0.4	2	0.05	1	0.3	0.5	0.01	0.01	0.3	0.01	0.2	0.7	0.6	0.1	2	0.01
Min (mg/kg)	0.021	0.0153	0.0162	0.0098	0.08	0.01	0.028	0.017	0.0101	0.0112	0.0516	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
MAX (mg/kg)	0.136	0.595	0.0518	0.0693	0.096	0.02	0.391	0.062	0.0947	0.0578	0.0549	0.03	1.5	0.028	0.012	0.013	0.0497	0.03	0.059
Frequency	14	8	8	7	4	4	3	3	2	2	2	1	1	1	1	1	1	1	1
Contaminated samples[a]			51																
Irregular samples		NA[b]	48																
		>MRL[c]	24																

[a] Presence of at least one pesticide residue ≥ LOQ.
[b] Pesticide not registered on loquat in Lebanon.
[c] Comparison with EU-MRL as no Codex-Alimentarius values are listed.
[d] (European Commission, 2020).

carbendazim, and thiametoxam are banned in Lebanon, their residues levels were below the MRLs set by the EU. In contrast, methomyl and dimethoate residues levels were higher than the LOQ = 0.01 mg/kg, which is the set MRL when the pesticides are disapproved in the EU. Similar pesticides residues, with different frequencies, were detected within the Food and Drug Administration (FDA) pesticide residue monitoring program fiscal year 2017 on 4270 samples of imported commodities and were listed as follows in percent of the total samples tested: cypermethrin (4.7%), dimethoate (2.2%), methomyl (1.1%), carbendazim (7%), and thiametoxam (6%) (U.S. FDA, 2019).

Loquat is one crop that currently has no MRLs set in the Codex Alimentarius (FAO/WHO, 2017). Consequently, the EU data base on MRLs (European Commission, 2020) was used for comparison of the detected residues levels from our survey. Pesticides encountered, such as flutriafol (5.4%), cyflufenamid (3.1%), chlorpyrifos (2.3%), tebuconazole (1.5%), tetraconazole (<1%), lambda-cyhalothrin (<1%), isopyrazam (<1%), myclobutanil (<1%), deltamethrin (<1%), thiophanate-methyl (<1%) are not authorized because they have never been registered for use in Lebanon on loquat (Table 3). Nevertheless, their residue levels did not surpass the EU-MRLs, and they could have been considered safe and conforming with the standards. Other pesticides, such as: mandipropamide (1.5%), azoxystrobin (1.5%), metalaxyl (<1%), and cymoxanil (<1%), were considered unauthorized as they were not registered for use on loquat by the EU and their residues levels surpassed the 0.01 mg/kg MRL.

Co-occurrence of pesticides residues is common when controlling a multitude of pests as confirmed in the results of the EU monitoring program on pesticides residues in human food conducted in 2016 (EFSA, 2018). Multiple residues of pesticides were found in 23 (17.9%) of the 128 tested samples. One sample of the 128 tested samples had up to 4 pesticides residues (mandipropamide + difenoconazole + dimethoate + tebuconazole). Ten (7.8%) samples included a combination of residues of 3 pesticides (2 scab fungicides and one insecticide or 2 insecticides and 1 fungicide). Twelve (9.4%) samples comprised residues of 2 pesticides: one scab fungicide and one insecticide. Similar results were recorded by Ramadan et al. in his survey on 10 vegetables (Ramadan et al., 2020). Four samples included the presence of technically unjustified residues of some pesticides, like mandipropamide or azoxystrobin, co-occurring with residues of difenoconazole. This might be explained by the fact that growers could have sprayed commercial formulations made of 2 active ingredients because they only contained difenoconazole, disregarding the fact that these combinations included also other irrelevant pesticides in the control of loquat pests. Other unjustifiably found pesticides residues were those of cymoxanil and metalaxyl that are not known to control any of the common pests listed on loquat in Lebanon. In turn, these results signal the importance of promoting extension and the training of growers on the safe and effective use of pesticides. Moreover, the necessity of facilitating pesticides registration and setting MRLs on minor crops is brought in front as is the case in other countries (Yang et al., 2016).

4.2. Dissipation studies

The results of the dissipation trials showed that penconazole 10% EC sprayed at the same rate of 50 ml of penconazole 10% EC/100 L of water on both apples and loquat under commercial field conditions dissipated following a first order kinetic dissipation model (Fig. 1).

The correlation coefficients varied between the 2 curves and ranged from 0.869 to 0.966, showing a very good fit to a first order model despite the variations attributed to the uncertainties concurrent with field trials. These results are in agreement with many published studies conducted on penconazole dissipation on tomatoes (Abd-Alrahman & Ahmed, 2012; Cabizza, Dedola, & Satta, 2012; Romeh, Mekky, Ramadan, & Hendawi, 2009), on other crops (Abd-Alrahman & Ahmed, 2013; Hem et al., 2011; Zhang et al., 2019), and on dissipation of other triazoles on apples (He et al., 2016; Szpyrka & Walorczyk, 2017; Yu

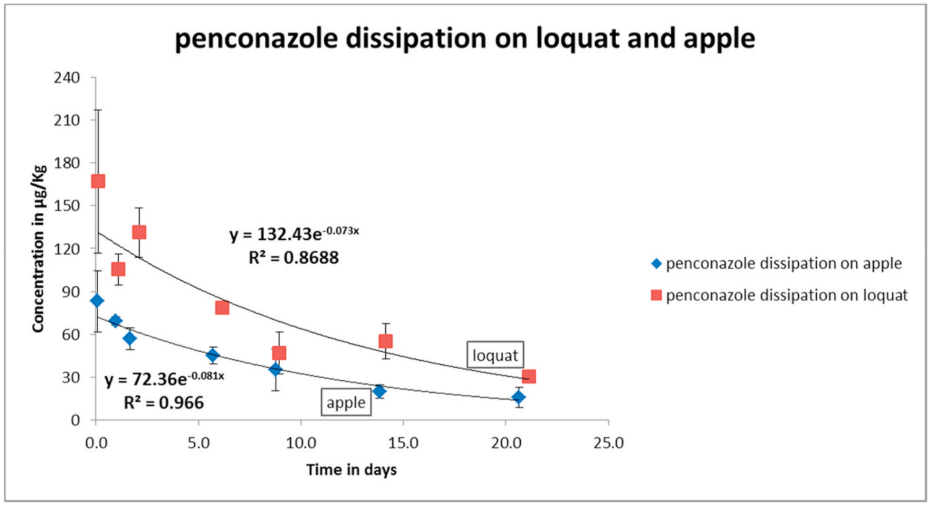

Fig. 1. Dissipation of penconazole on apple and loquat.

et al., 2011).

The absolute values of the slopes (K) varied between 0.073 and 0.081, showing a faster dissipation in apple compared to loquat. This might be explained by the different prevailing climatic conditions, mainly temperature, where the temperature range (9–20 °C) recorded during the loquat dissipation trial was relatively lower than the temperature range (19–29 °C) during the apple dissipation trial (Alister, Araya, Becerra, Saavedra, & Kogan, 2017; Fantke, Gillespie, Juraske, & Jolliet, 2014; Farha, Abd El-Aty, Rahman, Shin, & Shim, 2016; Marín, Oliva, Garcia, Navarro, & Barba, 2003).

The comparison of residue levels at 6 days with those of the initial deposits in the 2 dissipation trials shows a higher dissipation of penconazole in loquat (53.1%) than in apple (46.1%).

By the 14th day of the trials, penconazole degraded by 76% in apple and 67% in Loquat. At day 21, residues of penconazole were still detected at levels of 20 µg/kg in apple and 55 µg/kg in loquat but with values below the values of the EU-MRL of 0.1 mg/kg set on apple and 0.07 mg/kg set on loquat (Alister et al., 2014). The half-life calculated on apple and loquat were 8.56 days and 9.49 days respectively with a difference of only about one day.

4.3. Normal studies

Following the GAP of Lebanon, the initial deposit (C_0) of penconazole 10% EC on apple did not show residue levels above the adopted 0.1 mg/kg MRL set by the Codex Alimentarius, except for the trial conducted on the Golden delicious variety in Aammiq-Bekaa. Similarly, the initial residues concentration (C_0) derived from the loquat trials were below the 0.07 mg/kg MRL set by the EU, except for the trial conducted on the "Baladi" variety in Zoghdrayah where the initial deposit went way beyond the MRL (Table 4).

Table 4
Initial residue concentrations at 0 + 2 h and 14 days.

trial #	Varieties	Concentration at 0 + 2 h s in µg/kg	Concentration at 14 days in µg/kg
Apple			
1	Golden delicious	131 ± 20	62.5 ± 9
2	Super chief	59.5 ± 8	24 ± 3
3	Golden delicious	78.5 ± 19	51.5 ± 4
4	Scarlet spur	33.5 ± 4	12.5 ± 1
5	Double red	61.5 ± 8	22.5 ± 1
Diss	Red starking	93 ± 21	20 ± 5
Loquat			
6	Turkish	46 ± 2.83	22.5 ± 10.5
7	Spanish	57 ± 0.014	LOQ
Diss	Baladi	167 ± 50	55 ± 12

Variations in initial residue levels at 0+2 h between apple and loquat can be explained by differences in fruit size (surface to volume ratio), while variations in residue concentration at other intervals can be attributed to factors affecting dissipation rate, mainly: different crop growth dilution or apparent dilution and different prevailing weather conditions.

Residue levels of penconazole at 14 days of both apple and loquat trials were shown to belong to the same population, after conducting a Mann-Whitney *U* test that revealed a p-value = 0.714 > 0.05 (the significance level). Accordingly, individual residue datasets from the 6 trials on apple and individual data sets from the 3 trials on loquat, reflecting the same cGAP will be compiled (FAO, 2016). Therefore, residue data sets can be grouped and a preliminary MRL of 0.1 mg/kg can be adopted in Lebanon at the same GAP for both apple and Loquat as penconazole is already registered in Lebanon on apple. Nevertheless, none of the loquat trials showed at 14 days residue levels of penconazole exceeding the EU-MRL of 0.07 mg/kg. Accordingly, a preharvest interval (PHI) of 14 days can be proposed for loquat with a MRL of 0.07 mg/kg with the same GAP practiced on apple.

Farmers should not be trapped between official negligence and the reluctance of the suppliers to register their pesticides on minor crops because of the lack of justified return. The government should take the initiative to expand the registration not only of the other triazoles already registered on apple to include loquat, but also to expand the registration of all the pesticides on a commodity group representative to other minor crops in that group. Nevertheless, all of this must be done gradually within a program of supervised field trials to set MRLs of registered pesticides on minor crops.

5. Conclusion

This study has identified a range of unauthorized pesticides used on loquat produced in Lebanon. Presumably, the same issue is faced with other minor crops, such as berries, avocado, and persimmon. Unfortunately, no pesticides are registered on these crops, which have the potential to be exported to markets that are more and more restrictive in terms of pesticides residues. Furthermore, this study showed that penconazole behaved similarly on both apple and loquat, dissipating following 1st order kinetics. Penconazole can be proposed as a safe chemical alternative to control scab on loquat, with PHI of 14 days and a MRL = 0.07 mg/kg, following the same GAP adopted for apple.

A safe chemical management on minor crops necessitates monitoring programs directed towards minor crops, MRLs setting through bridging studies to make the registered pesticides on crop groups representatives available for use on minor crops, along with training programs for farmers on Integrated Pest Management and the safe and effective use of only the authorized pesticides.

CRediT authorship contribution statement

Mohamad I. Abou Zeid: Conceptualization, Methodology, Formal analysis, Investigation, Resources, Data curation, Writing – original draft, Visualization. **Mireille Kallassy Awad:** Validation, Data curation, Writing – review & editing, Supervision, Project administration. **Khalil C. Melki:** Formal analysis, Writing – review & editing, Visualization. **Yusuf Abou Jawdah:** Validation, Formal analysis, Data curation, Writing – review & editing, Supervision, Project administration. **Adla M. Jammoul:** Methodology, Validation, Formal analysis, Data curation, Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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